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In this work, we tested the possibility to use voltammetry for the evaluation of the area of solid electrodes. In the first step of the research study we adopted two voltammetric techniques, well known in the literature: i) cyclic voltammetry (CV) at different scan rates, followed by processing of the peak height with the Randles-Sevcik equation; ii) linear sweep voltammetry (LSV) at different electrode rotation rates, followed by data treatment with Levich equation[1,2]. The ferrocene/ferrocenium redox system was chosen as a probe for its well-known reversible process of diffusion-controlled single electron transfer. Acetonitrile and tetrabutylammonium esafluorophosphate were used as solvent and supporting electrolyte respectively. Initially attention was focused on a solid gold electrode (SGE). The evaluation of its area was made both on the electrode as received, without applying any treatment, and after a drastic surface treatment, to compare the effect of mechanical polishing on the measured area. The results obtained showed that such a treatment gave rise to a significant decrease of the standard deviation of the results and a decrease of the value measured for the area. Method i) was then applied to a glassy carbon electrode (GCE) in three different conditions: unmodified and modified with an Au-film (AuF-GCE) and with an Au-nanoparticle layer (AuNP-GCE), to investigate the influence of the "roughness" of the electrode surface on the value measured for the area. According to the literature, the above-mentioned electrochemical techniques should respond to the electrode projected areas[2,3]: however, we found that the measured areas differ for each modification, suggesting that the morphology of the active surface influences the results of the calculation. Subsequently, method i) was applied to home-made carbon paste electrodes (CPE) of different sizes, to test the relationship between the diameter of the electrode body and the measured area. The calculated areas were compared with those obtained by recording electrode images by scanning electron microscopy (SEM) and processing the data with Wolfram Mathematica software. In the second step of the study, the actual active surfaces of the SGE and of the two Au-modified GCEs were estimated by CV in H_2SO_4, from the areas of the cathodic peak obtained in each voltammogram, through the theoretical charge associated with the reduction of the oxide layer per unit surface area of gold[4]. In conclusion, voltammetry provides information on the area of solid electrodes, but, despite the notoriety of the equations considered in this study, there are some doubts about the kind of "area" actually involved in the measurement process; further studies are required to correctly interpret experimental results. Finally, the evolution of the SGE surface during an extended period of usage was checked by periodically recording cyclic voltammograms in H_2SO_4. Clear differences were observed in the CV curves over time and a relationship between the shapes of the voltammograms and the performance of the electrode was found: therefore, CV can be a used to monitor the state of the SGE surface and identify the need for a mechanical polishing or even a substitution of the electrode.

References
1. Brown R. J. C. and Milton M.J.T.; *IEEE Transactions on Instrumentation and Measurement*, 2007, *56*, 280-283.
2. Bard A. J. and Faulkner, L.R.; "Electrochemical Methods. Fundamentals and Applications", 2° Edition, J. Wiley & Sons, New York, 2001.
3. Neghmouche N. S. and Lanez T.; *Recent Trends in Physical Chemistry an International Journal*, 2013, *1*, 1-3.
4. U. Oesch and J. Janata; *Electrochimica Acta*, 1983, *28*, 1247-1253.